

THE OXIDATION OF CVD SILICON CARBIDE IN CARBON DIOXIDE

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Abstract

Chemically-vapor-deposited silicon carbide (CVD SiC) was oxidized in carbon dioxide (CO₂) at temperatures of 1200-1400°C for times between 100 and 500 hours at several gas flow rates. Oxidation weight gains were monitored by thermogravimetric analysis (TGA) and were found to be very small and independent of temperature. Possible rate limiting kinetic laws are discussed. Oxidation of SiC by CO₂ is negligible compared to the rates measured for other oxidants typically found in combustion environments: oxygen and water vapor.

Introduction

SiC-based composites are currently being developed for use in the complex environments of heat engines. Possible degradation mechanisms for SiC in combustion environments have been reviewed by Jacobson [1]. Fuel-lean combustion environments typically contain unburned oxygen as well as the

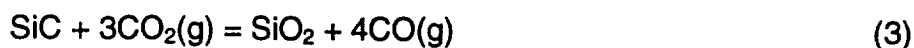
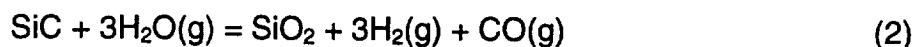
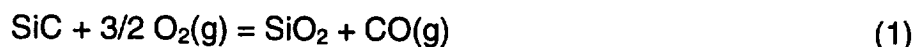
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Presented at the 98th Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 1996: Paper C-30-96.

gaseous products of water vapor and carbon dioxide. The behavior of SiC in oxygen has been well studied [1]. Much work has also been done to understand the effects of water vapor on SiC [2-4]. Limited work, however, has been conducted on the oxidation of SiC in carbon dioxide.

In a combustion environment, oxidation of SiC can occur by any of the following reactions:



In each case solid silica is formed with the generation of gaseous products. The determination of both the rate law and the relative rates of oxidation for each reaction is important in predicting the behavior of SiC in combustion environments.

The oxidation of SiC in pure oxygen is known to follow a linear parabolic rate law [1] which can be expressed simply as:

$$x^2 + Ax = B(t + \tau) \quad (4)$$

where x is oxide thickness, t is time, B is the parabolic oxidation rate constant hereafter referred to as k_p , B/A is the linear oxidation rate constant hereafter referred to as k_l , and τ is a time correction factor to account for any oxide present on the surface initially. At short times and low temperatures linear oxidation

kinetics are observed, indicating that oxidation is rate limited by the reaction of oxygen at the SiC surface. The limiting case of Equation 4 is observed

$$x = k_l t \quad (5)$$

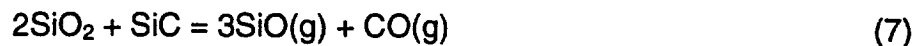
At long times and high temperatures simple parabolic kinetics are observed, indicating that the oxidation rate is controlled by transport of oxygen through the growing oxide scale. The other limiting case of Equation 4 operates

$$x^2 = k_p t \quad (6)$$

Silica formation from SiC in water vapor also follows linear parabolic rates laws as observed in oxygen [4] but with more complicated parabolic kinetics at high water contents and higher gas velocities due to the formation of a volatile hydroxide, Si(OH)_4 [3,5].

The oxidation of SiC in CO_2 has been limited to a few studies conducted before the availability of high purity stoichiometric CVD SiC. Lea [6] found that SiC gained weight in pure CO_2 with parabolic-like kinetics (e.g. the oxidation rate decreased with time). Antill and Warburton [7] reported parabolic rate constants for SiC oxidation in pure CO_2 although no weight gain kinetic curves are shown. The oxidation rate was about twenty times slower in CO_2 than in O_2 , independent of CO_2 partial pressure, while the temperature dependence for the oxidation rate was found to be the same as for oxygen. Fitzer and Ebi [8] show parabolic-like kinetics for SiC in CO_2 up to temperatures of 1500°C . At higher temperatures and lower CO_2 partial pressures in nitrogen parabolic kinetics are observed.

Weight losses after initial weight gains are attributed to a reaction at the SiC/SiO₂ interface:



Finally, Bremen et al [9] studied SiC exposed in CO/CO₂ mixtures. Oxide thicknesses were found to decrease as the amount of CO₂ increased in the gas mixtures. A silica scale thickness of 0.61 μm was reported for a sample exposed in pure CO₂ at 1350°C for 275h although the oxidation kinetics are not shown.

The contributions of this work are as follows. First, the oxidation rate of high purity stoichiometric CVD SiC in CO₂ is reported for the first time. Second, the rate limiting mechanism for oxidation in CO₂ is discussed. Finally, the oxidation rates of SiC in CO₂ are compared to rates observed for other oxidants found in combustion environments, i.e, oxygen and water vapor.

Experimental Procedure

CVD β-SiC (Morton International) coupons were used for all tests. A sample purity of 99.999% is reported by the manufacturer. In addition, the SiC is stoichiometric (Si to C ratio equal to one) as determined by a gravimetric method which is sensitive to a fraction of a percent [10]. Sample coupons of about 2.5 x 1.0 x 0.3 cm and a surface area of about 7.5 cm² were used for all tests. All samples were cleaned in detergent, DI H₂O, acetone, and alcohol prior to testing.

Samples were suspended with sapphire hangers from a microbalance (Cahn 1000, Cahn Instruments, Cerritos, CA) within a 2.2 cm inner diameter fused quartz reaction tube in a furnace with molybdenum disilicide heating elements. Fused quartz tubes were used to minimize impurity enhanced oxidation of SiC [11]. CO₂ was dried with CaSO₄ and flow rates through the tube were controlled with a flow controller (Tylan General, Torrance, CA). The system was closed and flushed with CO₂ for varying times prior to the initiation of oxidation.

Temperatures were calibrated using a Type R thermocouple in the sample position in separate experiments so that impurities due to alumina thermocouple sheaths were not present during the oxidation exposures. Oxidation was initiated by raising the furnace, already at temperature, from a lower position to one in which the hot zone was positioned around the sample. Weight change and time were acquired digitally. The ranges of temperatures, flow rates, flush times, and exposure times are summarized in Table 1. X-ray diffraction analysis (XRD) was conducted for selected samples after oxidation.

Results

Weight changes were found to be very small, varying between 0.9×10^{-2} and 3.7×10^{-2} mg/cm² and averaging 2.1×10^{-2} mg/cm². These weight gains correspond to silica thicknesses of 0.12 to 0.48 μm, with an average thickness of 0.27 μm. The results are summarized in Table 2. Several typical weight change curves are shown to times of 100h in Figure 1a and to times of 500h in Figure 1b. No time dependence, temperature dependence, flow rate dependence, or

dependence on flush time prior to initiation of oxidation could be determined. The lack of correlation is shown in Figures 2 and 3.

The weight gain and oxide thicknesses reported in the previously described studies are all higher than those reported in this study. This is understandable considering the higher purity SiC material used in this study as well as the clean oxidation environment. The nearest oxidation rates are those reported by Antill and Warburton [7] who reported parabolic rate constants corresponding to 0.3 to 0.5 μm oxide thicknesses for 100 hour exposures at 1200 and 1300°C, respectively.

Samples exposed to CO_2 at 1200°C showed interference colors typically observed for thin amorphous silica layers. XRD confirmed the presence of SiO_2 on a sample oxidized at 1400°C where crystalline SiO_2 is expected as shown in Figure 4.

The weight change of CVD SiC in various gaseous environments at 1200°C is compared in Figure 5. Results up to 20 hours are shown so that the effects of silica volatility in 50% H_2O /50% O_2 are negligible. Parabolic rate constants for SiC oxidation are on the order of $1 \times 10^{-3} \text{ mg}^2/\text{cm}^4 \text{ h}$ in 50% H_2O /50% O_2 [4] and $1 \times 10^{-4} \text{ mg}^2/\text{cm}^4 \text{ h}$ in O_2 [12] at 1200°C. If the average weight gain for SiC in CO_2 at 1200°C is force fit to a parabolic rate law, k_p would average $3 \times 10^{-6} \text{ mg}^2/\text{cm}^4 \text{ h}$.

It can be seen that weight gains due to oxidation by CO₂ are insignificant compared to those from the other oxidants present in combustion environments.

Discussion

CO₂/CO gas chemistry effects

The gas used in these experiments was pure CO₂ and was thus an unbuffered system. At high temperatures CO₂ will decompose a small amount. This was calculated to vary between 0.03 and 0.17% CO using ChemSage [13]. The resulting oxygen partial pressures varied between 3×10^{-4} and 9×10^{-4} atm. These oxygen partial pressures are higher than those needed for active oxidation of SiC [14]. In addition, active oxidation of SiC in mixed oxidizing/reducing gases has been shown to depend on oxidant partial pressure (i.e. CO₂ partial pressure) rather than oxygen partial pressure [14]. Additional evidence that active oxidation is not occurring is that changing the gas velocity by an order of magnitude did not affect the observed weight changes. Weight losses were not observed at long times.

Uncertainty due to TGA technique

Drift of the microbalance voltage output which corresponds to the weight change is a major concern for these measurements. Typically drift in this signal is on the order of magnitude of 0.1 mg loss in 100 hours and is somewhat linear. This is the same order of magnitude of the measured weight gains of the SiC samples. To account for this drift, a linear drift rate was assumed and the final sample

weight as measured by the TGA was fixed to that measured by a bench top balance. Thus the shape of the kinetic curves is suspect since it depends on the assumption of linear drift.

Buoyancy effects may also have an effect on the initial weight changes. There are two effects to consider here. First, as the gas temperature increases the sample will have an apparent weight loss. Second, as any residual air is flushed out of the tare side of the balance an apparent weight gain of the sample will occur due to differences in density of air and CO_2 . While both these effects are small, they are significant when such small weight gains occur and when the shape of the weight change vs. time curve is interpreted to establish rate limiting steps.

Residual air in the balance chamber may have more than an effect on buoyancy. It may also affect the oxidation rate. Since oxidation rates in CO_2 are so small, trace amounts of oxygen in the gas stream may account for significant amounts of oxide formation. At the standard flow rate of 100ccm, it should take 6 minutes to flush out the furnace tube, however, residual air may remain in the balance chamber for longer times. The weight gain was plotted as a function of flush time in Figure 3 and no correlation could be seen. In addition, higher flow rates (faster flushing) did not result in lower weight gains. However, one experiment was conducted in a TGA equipped with a mechanical vacuum pump. The complete volume was evacuated and filled with CO_2 several times before

oxidation. This experiment resulted in the lowest weight gain. This suggests that residual oxygen in the system may be responsible for the variability of the results.

Oxidation Rate Limiting Step

Oxidation reactions can be limited by transport of oxidant or gaseous products through gas boundary layers, by diffusion of the oxidant through the oxide, by dissociation at the reaction interface, or by the chemical reaction at the interface. The low weight gains observed in this study make a definitive determination of the rate determining step difficult, but the evidence supporting or refuting each possibility can be discussed.

Transport of gas species through a boundary layer is dependent on the square root of the gas velocity. Because the oxidation rates of SiC in CO₂ were insensitive to gas flow rates varying between 100 and 1000ccm this possibility is unlikely. This independence of oxidation rate from gas velocity also indicates that surface active oxidation to SiO(g) formation is not occurring.

Diffusion limited oxidation results in parabolic oxidation rates. In the case of SiC oxidation in CO₂, it is expected that molecular permeation of CO₂ through silica would occur in analogy to molecular permeation which occurs in oxygen. While CO₂ is larger than O₂ (3.94Å vs. 3.47Å), CO₂ is a product of SiC oxidation in oxygen and has not been found to limit oxidation in pure O₂. Both the kinetic

curves in Figure 1 and the end point weights plotted vs. time in Figure 2 do not show parabolic behavior. An initial weight gain is observed with relatively constant or slightly decreasing weight at longer times. In addition, diffusion is typically a relatively highly activated process. The lack of temperature dependence observed here indicates a lower activated process may be rate controlling.

Surface reaction limited oxidation shows linear rates. Two types of surface reactions can limit oxidation. First, dissociation of CO_2 to CO and an oxygen species must occur. Then the oxygen must react with the SiC. Because we know oxygen reacts readily with SiC from experiments in oxygen, it seems more likely that the low rates observed in this study would be due to CO_2 dissociation. Childs and Wagner [15] report that for the oxidation of iron, the CO_2/CO surface reaction is slower than the $\text{H}_2\text{O}/\text{H}_2$ surface reaction. It is probable that this holds true for the oxidation of other materials. From earlier work [4] it was found that linear reaction rates of H_2O with SiC are significantly slower than oxygen at 1100°C . Thus it seems likely that linear reaction rates of CO_2 with SiC might limit oxidation at temperatures higher than 1100°C . Diffusion is usually more temperature dependent process than surface reactions, so that the lack of temperature dependence observed here may indicate surface reaction control of SiC oxidation in CO_2 . The shape of the kinetic curves shown in Figures 1 and 2 do not support linear kinetics. As already discussed, it is difficult to confidently

say that oxidation of SiC in CO₂ follows any particular rate law given the limitations of the thermogravimetric technique for such small weight changes.

Fitzer and Ebi [8] proposed that the interface reaction (Equation 7) occurs and is responsible for observed weight losses in 100 % CO₂ at 1525°C and at lower temperatures in N₂/CO₂ mixtures. This reaction has been studied by Jacobson, Lee, and Fox [16]. It may be possible that the reduced amount of CO formed by the oxidation reaction (Equation 3) due to kinetic limitations (dissociation of CO₂) allows the interface reaction between SiC and SiO₂ (Equation 7) to occur. In some experiments conducted in the present study the weight change appeared to level off or decrease slightly at long times. However, under the conditions of this study, no evidence of overall weight loss was observed, similar to the results of Fitzer and Ebi under the same conditions. This interface reaction is not likely to occur in combustion environments where the oxidation rate of SiC by water vapor and oxygen is rapid.

Regardless of rate law model, this work demonstrates that oxidation of SiC in CO₂ is very slow, and that in a typical fuel-lean combustion environment the oxidation of SiC can be satisfactorily modeled by the oxidation rates of SiC in water vapor and oxygen.

Conclusions

Oxidation weight gains of SiC exposed to CO₂ at temperatures between 1200 and 1400°C were found to be very small and independent of temperature and gas flow rate. The rate limiting kinetic step for SiC oxidation in CO₂ could not be determined due to the low weight gains and the limitations of the TGA technique. Oxidation of SiC by CO₂ is negligible compared to the rates measured for other oxidants typically found in combustion environments: oxygen and water vapor.

Acknowledgments

The authors would like to thank Ralph Garlick for the XRD results and Don Humphrey for the vacuum TGA results.

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Table 1
Experimental Conditions for Oxidation of SiC in CO₂

Temperature (°C)	1200, 1300, 1400
CO ₂ flow rates (ccm)	100, 1000
exposure times (h)	100-500
flush times (h)	0.1 - 18.75

Table 2
Summary of Weight Gain Results for Oxidation of SiC in CO₂

Temperature (°C)	oxidation time (h)	CO ₂ flow rate (ccm)	CO ₂ flush time (h)	weight gain (mg/cm ²)
1200	96	100	0.9	1.31×10^{-2}
↓	100	100	2.5	2.09×10^{-2}
↓	100	100	1.0	1.08×10^{-2}
↓	100	100	0.3	2.48×10^{-2}
↓	100	100	0.1	2.24×10^{-2}
↓	500	100	0.6	3.66×10^{-2}
↓	100	1000	0.3	1.43×10^{-2}
↓	267	1000	18.75	2.21×10^{-2}
↓	100	100	vac/backfill	0.93×10^{-2}
1300	100	100	2.57	2.13×10^{-2}
↓	100	100	0.75	1.95×10^{-2}
↓	100	100	2.5	1.70×10^{-2}
1400	100	100	0.55	2.31×10^{-2}
↓	100	100	1.35	2.74×10^{-2}
↓	100	100	0.5	2.35×10^{-2}
↓	500	100	1.85	2.49×10^{-2}

List of Figures

Figure 1a. Oxidation weight change kinetics of CVD SiC in CO₂ for 100h as a function of temperature.

Figure 1b. Oxidation weight change kinetics of CVD SiC in CO₂ for 500h as a function of temperature.

Figure 2. Final measured weight changes of CVD SiC oxidized in CO₂ showing indeterminate time and temperature dependence.

Figure 3. Final measured weight changes of CVD SiC oxidized in CO₂ showing indeterminate dependence on initial balance flush time.

Figure 4. X-ray diffraction spectrum for a CVD SiC sample oxidized in CO₂ at 1400°C for 100h.

Figure 5. Oxidation weight change kinetics of CVD SiC in 50% H₂O/50% O₂ [4], O₂ [2], and CO₂ [this study] at 1200°C.

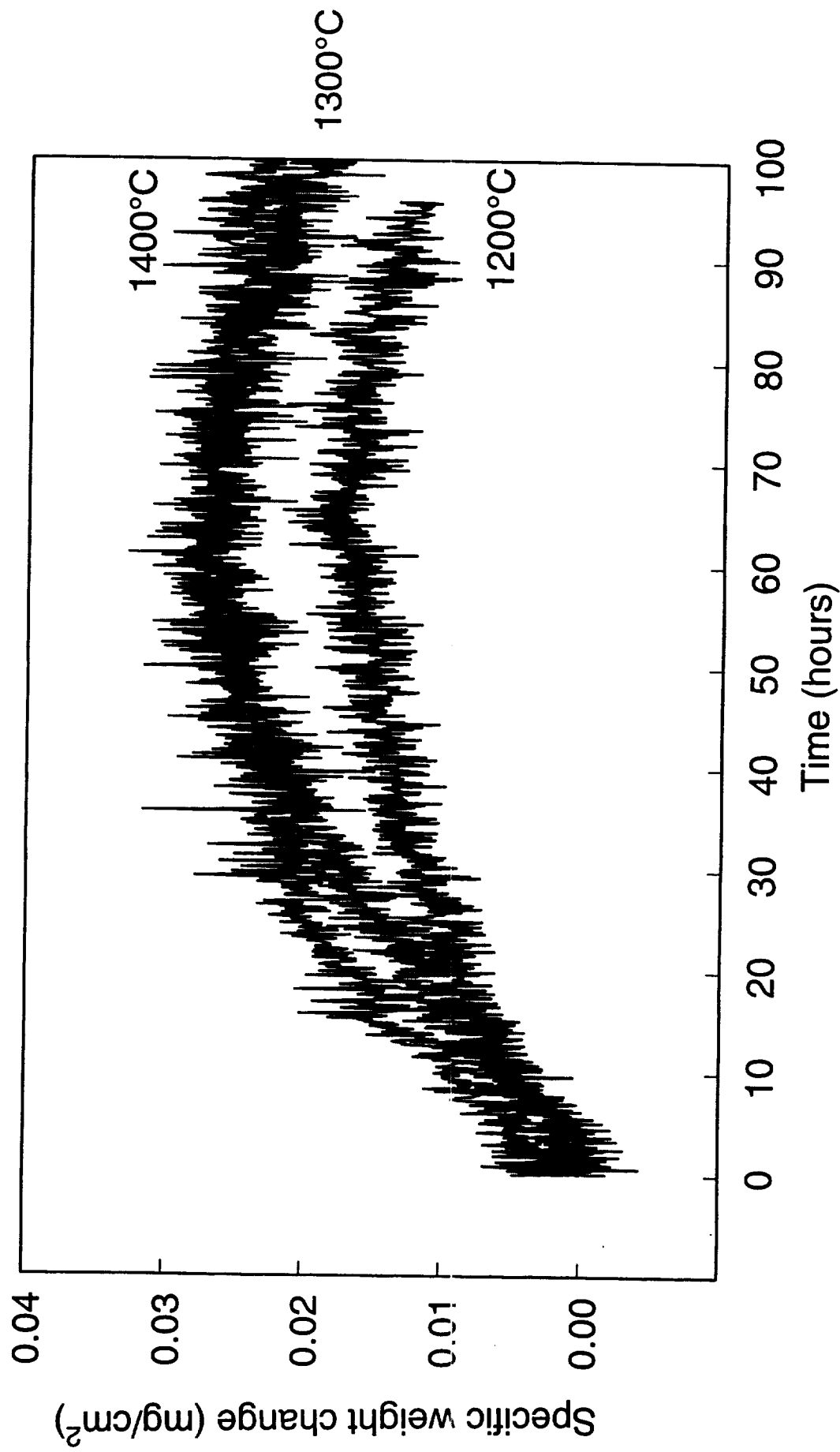


Fig. 1a

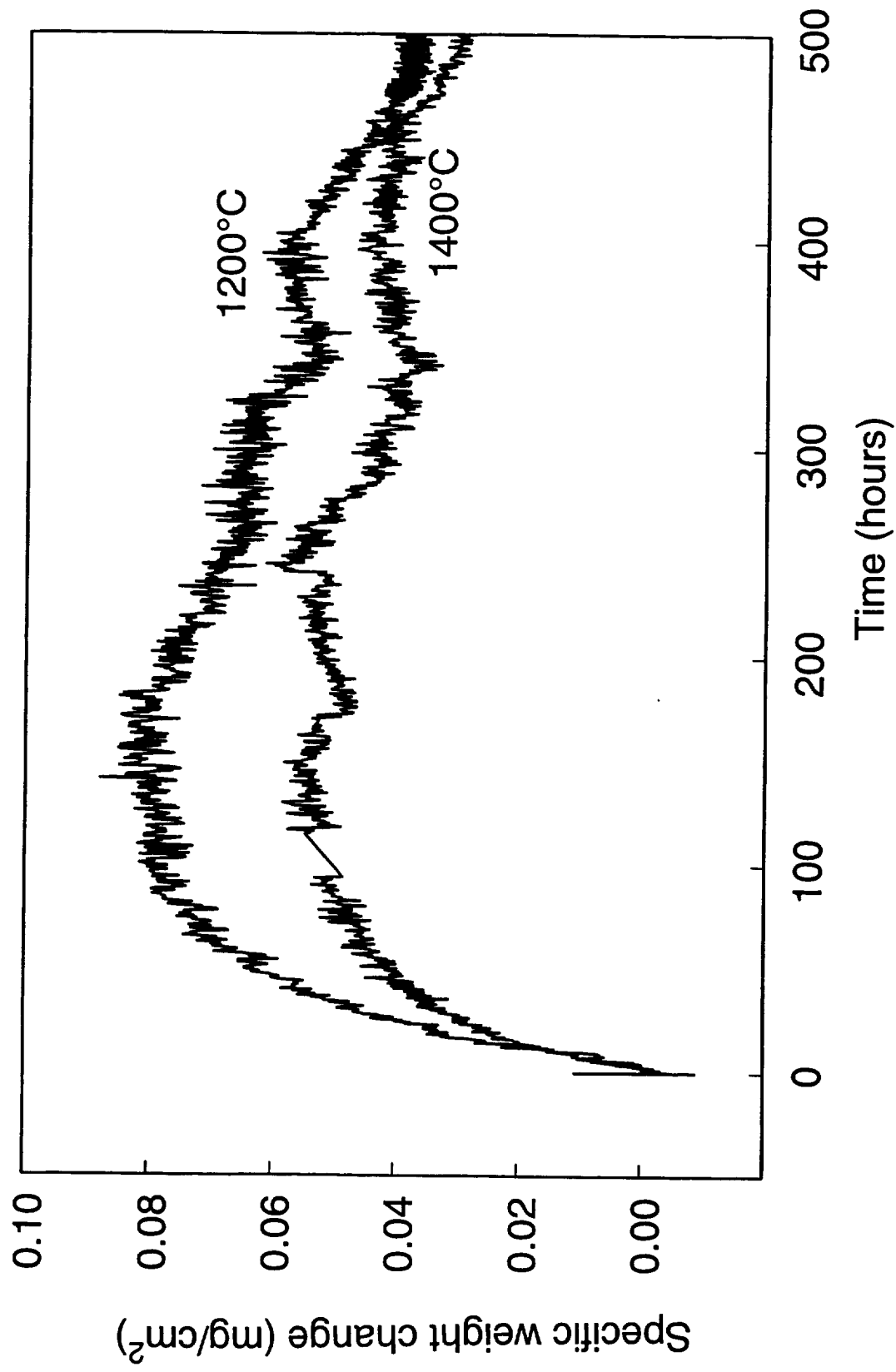


Fig. 1b

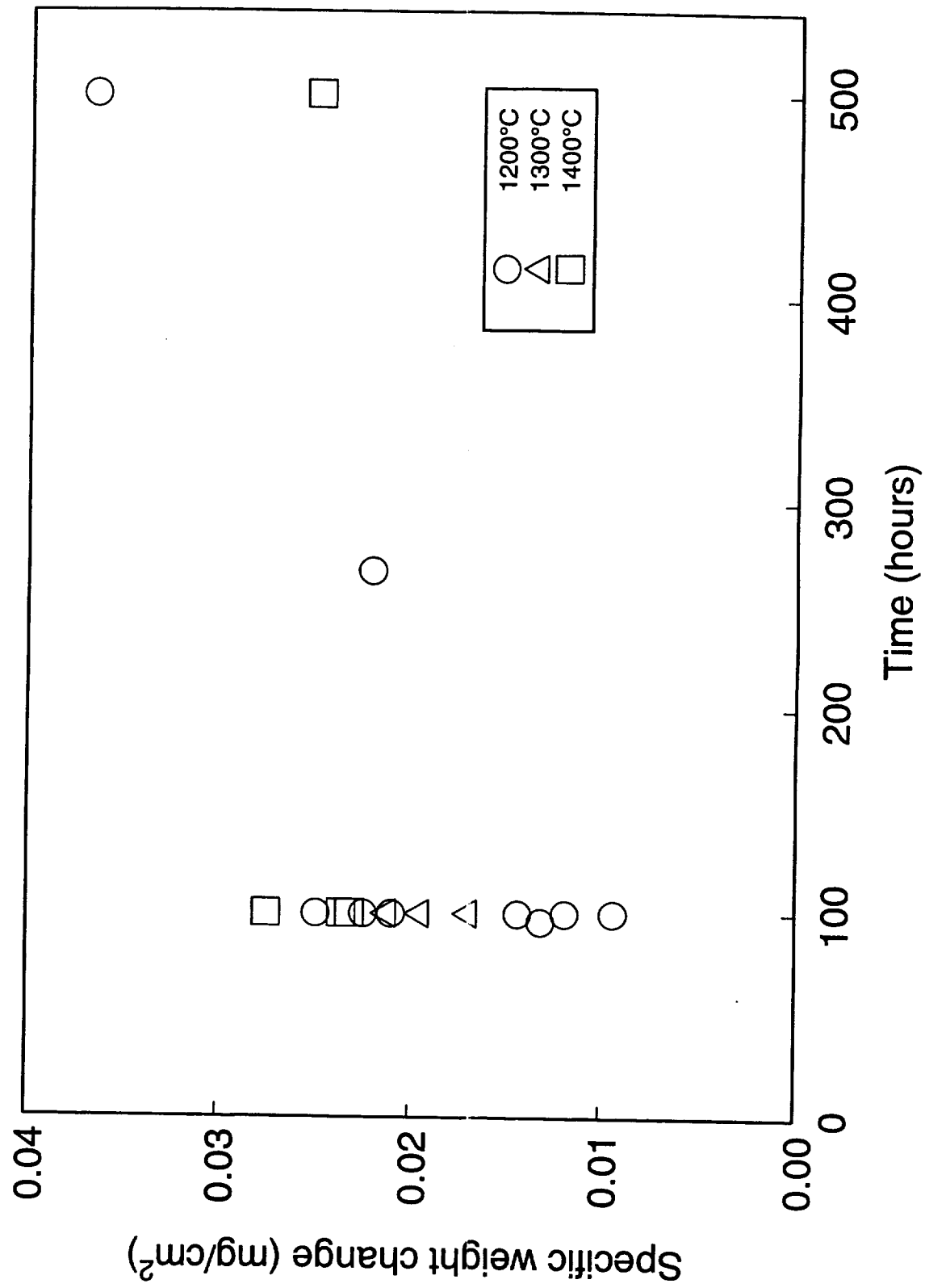


Fig. 2

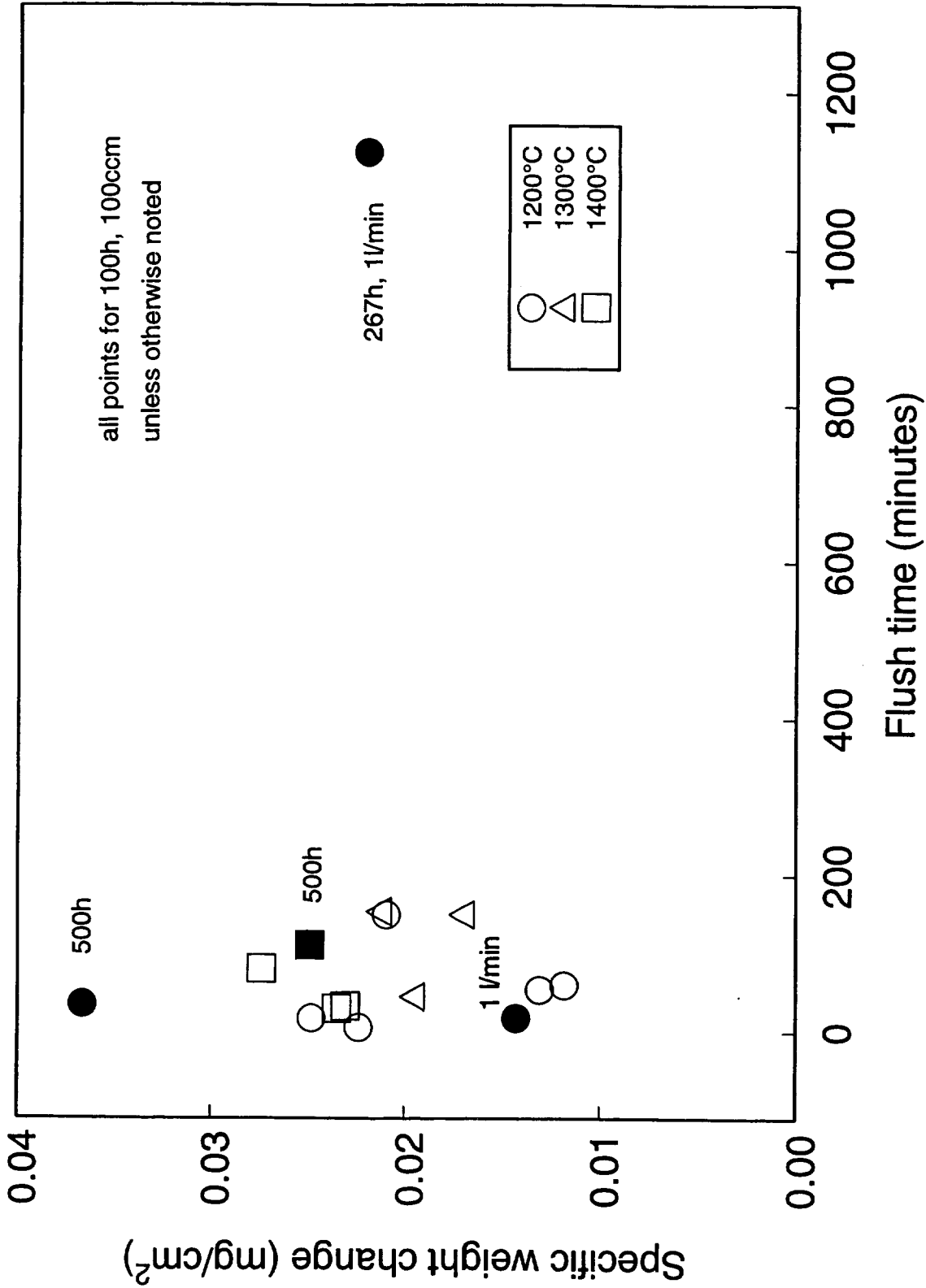


Fig. 3

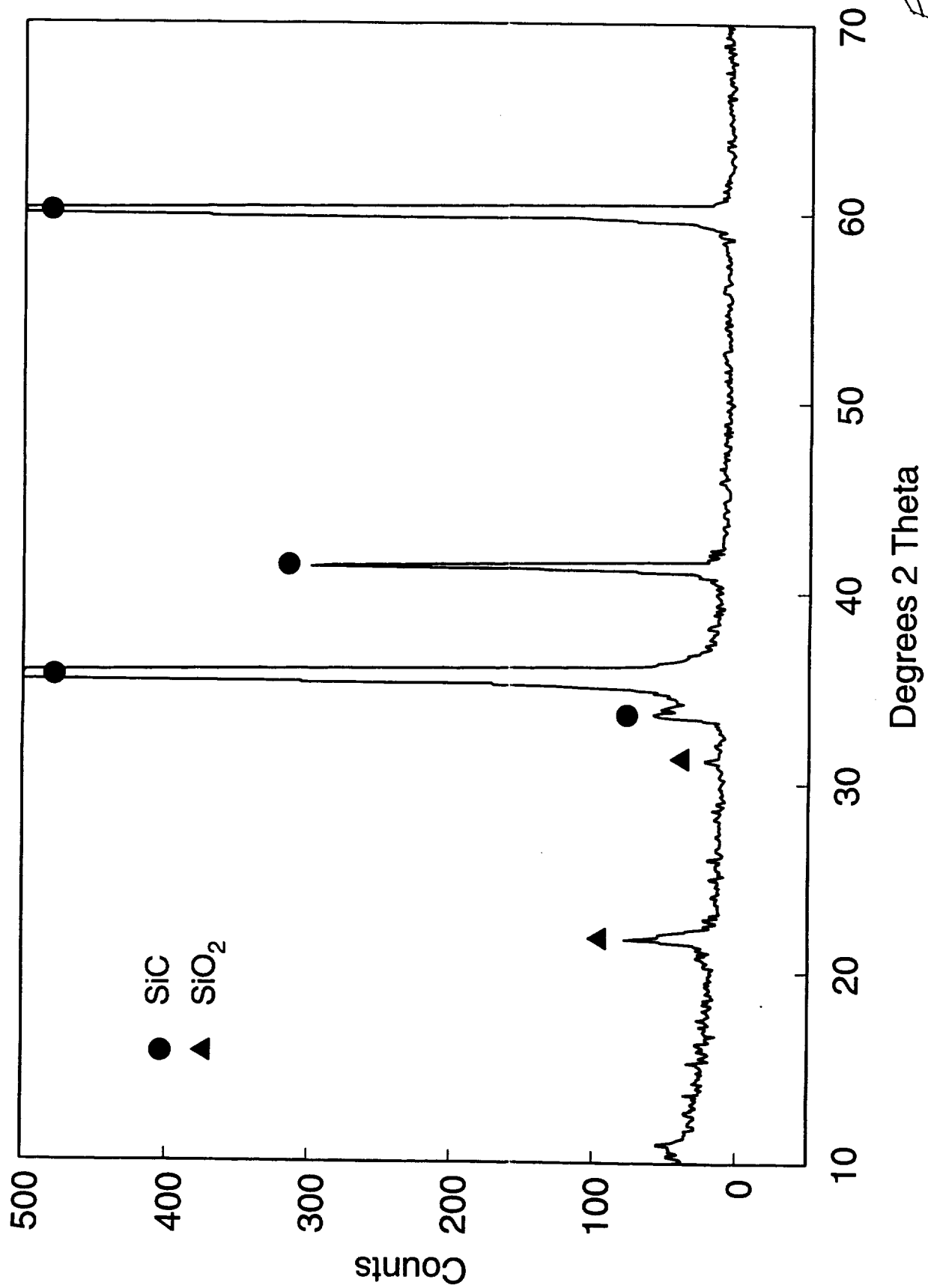


Fig 4

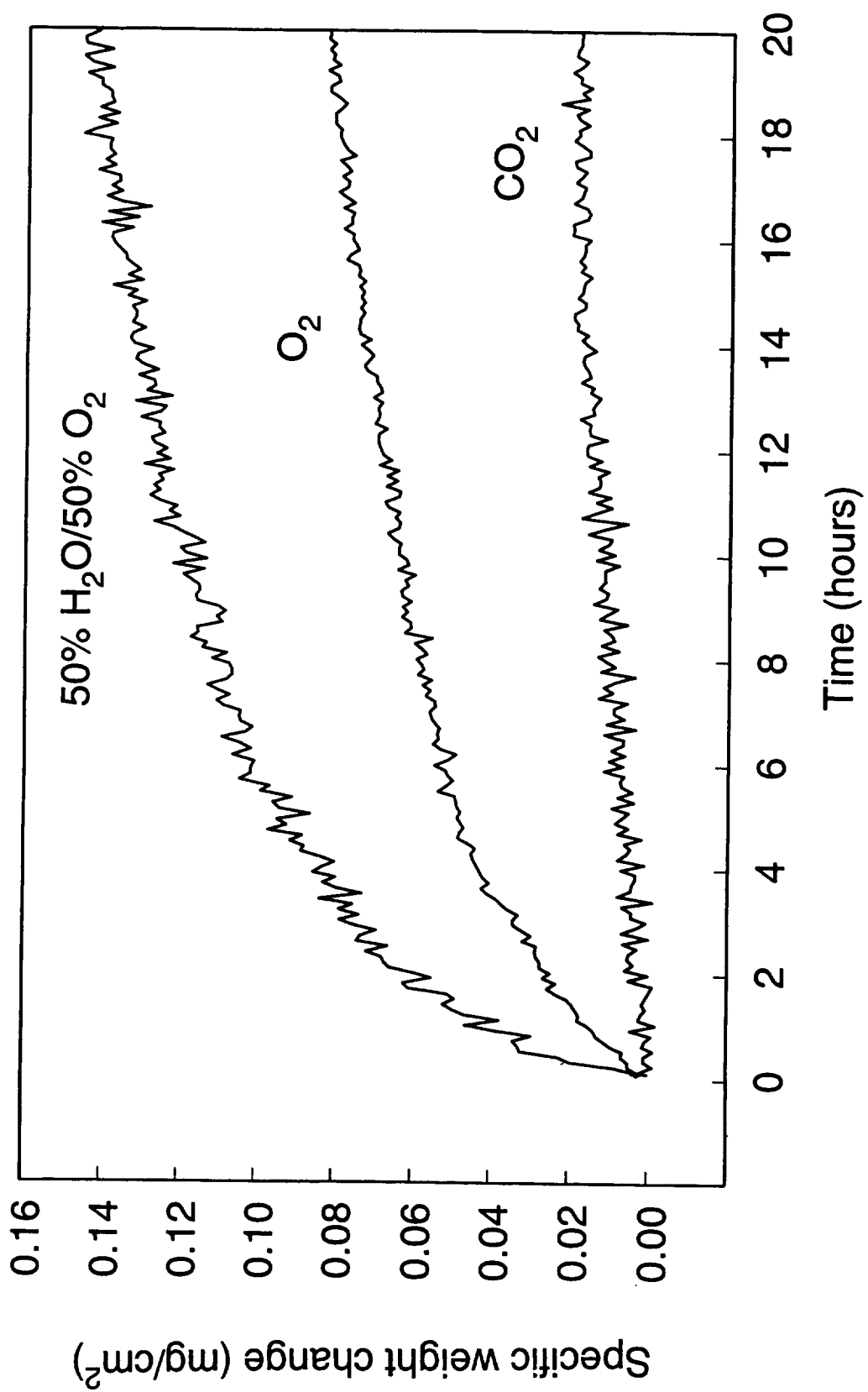


Fig. 5

